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FERROMAGNETIC BEHAVIOR OF Mn^{2+} DOPED TITANIA NANOTUBES

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ABSTRACT

Hydrothermal synthesis of Mn doped titanianantubes, which showed room temperature ferromagnetism (RTFM)is reported. Morphology of Mn doped nanotubes was characterized by transmission electron microscopy (TEM). The size of nanotubes was relatively uniform with outer diameter of about 10 nm and lengths of up to few hundred nanometers. The x-ray powder diffraction (XRPD) analysis of resultant powder confirmed the appearance of mixed crystalline phases inMn doped nanotubes: hydrogentitanate ($H_2Ti_2O_5$ x H_2O)and tetragonal anatasetitania. RTFM ordering with saturation magnetic moment (M_s) of the order of 1.27 μ_B per Mn atom was observed.

INTRODUCTION

The ability to control the spin of electrons in addition to their charge in diluted magnetic semiconductors would expand their applications in conventional electronic devices. The term diluted magnetic semiconductor (DMS) refers to a non-magnetic semiconductor material where the host cations are replaced with magnetic impurities up to a few atomic percent. DMSs were mostly based on II-VI or III-V compounds, butthose materials were unattractive for practical electronic applications, since ferromagnetism has been achievable far below room temperature [1]. Recently it was theoretically predicted that transition metal ions doped metal oxides (TiO_2, SnO_2, In_2O_3, ZnO) are suitable material for DMSs with ferromagnetic behavior at room temperature [2-4]. In this paper we reporteda novel method for the synthesis of Mn doped titania nanotubes as well as their structural and magnetic properties.

EXPERIMENTAL

All chemicals were reagent-grade from Aldrich and used as received. Mn doped titania nanotubes were synthesized according to Kasuga et al. using powder of 1 at.% Mn^{2+} doped anatase TiO_2nanoparticles as a precursor[5].The 1 at% Mn^{2+} doped TiO_2nanoparticles weresynthesized using the slightly modified synthetic procedure already reported [6, 7].For the synthesis of nanotubes, 250 mg of 1 at% Mn^{2+} doped TiO_2nanoparticles was dispersed in 10 ml 10 M NaOH and hydrothermally treated 20 h under saturated vapor pressure of water at 150 °C. After autoclaving, the ensuing powder of nanotubes was washed with distilled water until pH7. The powder was then air dried at 70 °C. Film for magnetic characterization was prepared by drop casting of dispersions of Mn doped nanotubes onto pre-cleaned glass substrate. The films were annealed in air for 2 min at 150 °C after each drop. The shape and size of Mn doped nanotubes were characterized using JEM 1400 transmission electron microscope operating at 120 kV. The XRPD pattern was obtained on a Philips PW-1050 automated diffractometer. The percent of Mn ions in nanotubes was determined using *inductively coupled plasma* (ICP) emission spectrometry. The concentration of Mn ions in the sample of titanianantubes was 0.016 at.% of the amount of Ti^{4+} ions. The field dependence of the magnetic moment was measured using a superconducting quantum interference device magnetometer (SQUID). Hysteresis loop measurement has been performed up to 60 kOe.

RESULTS AND DISCUSSION

Mn doped titania nanotubes were synthesized by hydrothermal processing of Mn^{2+} doped anatase TiO_2nanoparticles in proton deficient aqueous solution [5]. Conventional TEM image of the 0.016 at.%Mn doped titanianantubes is shown in Fig. 1. Uniform size distribution of nanotube diameters (d ~ 10 nm) was observed. The length of the nanotubes was in a wide range from one hundred to a few hundred nanometers. The nanotubes had an open-ended multiwall structure. Structural analysis of

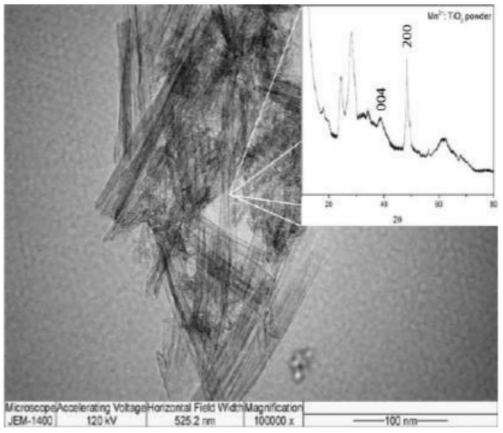

Figure 1. TEM image of Mn doped titania nanotubes; Inset: XRPD pattern

0.016 at.%Mndoped nanotubes, inset Fig. 1,revealed the presence of mixed crystalline phases in the sample. Diffraction peaks at 2θ = 24.5°, 28.1° and 34.1°confirmed the presence of hydrogentitanate ($H_2Ti_2O_5$ x H_2O), which usually appear in the samples of hydrothermally synthesized titania nanotubes, while the intense peak at 2θ = 48.5° and peak appearing at 38.7°could be indexed as diffractions from the anatase TiO_2 crystal planes (200) and (004)[8, 9].

The magnetic response for film made of 0.016 at.%Mn doped titania nanotubes as a function of magnetic field strength (H) was followed at room temperature. The field dependent magnetization after diamagnetic correction is shown in Fig. 2. As can be seen from Fig. 2,the ferromagnetic ordering with coercive field of Hc ~ 180Oe and M_s of the order of 1.27 μ_B/Mn, appeared in 0.016 at.% Mn doped titania nanotubes. Based on the experimental results and theoretical models it wasproposed that oxygen vacancies (F^+ centers)play an important role in mediating the magnetic ordering in oxide based DMS materials[10, 11]. It is known that RTFM of Mndoped TiO_2nanocrystals significantly depends on structural defects and only the F^+ centersin bulk mediates the FM ordering[10]. Titania nanotubes contain a large fraction of structural defects and majority of them is located on the interior walls of the nanotubes [9]. Also, Ahmed et al.showed that lower content of Mn^{2+} dopant ions (< 1 at. %) favors the ferromagnetic interaction while the higher concentrations of Mn^{2+} lead to the formation ofantiferromagneticordering of Mn^{2+}clusters[10]. Relatively high value of M_s in our sample is not only due tothe low concentration of Mn ionsbut also the presence of F centers should be taken into account. Our results indicatea high content of bulk F^+ centers in titania nanotubes and that the high fraction of Mn ionsinvolved in FM ordering.

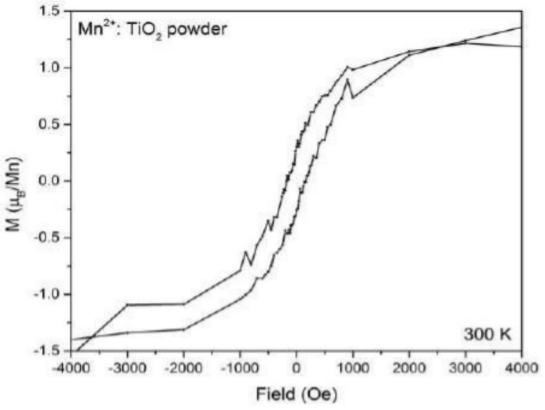

Figure 2. Magnetization curve for Mndoped titania nanotubes

CONCLUSION

The Mndoped titania nanotubes were synthesized applying hydrothermal treatment on proton deficient aqueous dispersion of 1 at.% Mn^{2+}doped

anatase TiO_2 nanoparticles. XRPD study confirmed that the nanotubes possesseda mixed phase crystalline structure. The $H_2Ti_2O_5$ x H_2Oandanatasecrystalline phaseswere detected in the sample. The ferromagnetic ordering at room temperature with closed loop (*Hc*~ 180Oe) and M_s of the order of 1.27 μ_B/Mn atom were observed in the film made of Mn doped titania nanotubes. The reason for observed ferromagnetism and relatively high value of *Ms*could be found in the high content of bulkoxygen vacancies (F^+ centers) and their interaction with the substitutional Mn impurity.

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